

# PATENT SPECIFICATION

(11) 1401089

1401089

- (21) Application No. 23361/73 (22) Filed 16 May 1973  
 (31) Convention Application No. 65373 (32) Filed 17 May 1972 in  
 (33) Luxembourg (LU)  
 (44) Complete Specification published 23 July 1975  
 (51) INT CL<sup>3</sup> A61K 7/06  
 (52) Index at acceptance

A5B 774

C5D 6A6 6B12B3 6B12F1 6B13 6B1 6B8 6C8

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## (54) COSMETIC COMPOSITIONS FOR STRENGTHENING HAIR AND PROCESS FOR THE TREATMENT OF HAIR

(71) We, L'OREAL, a French Body Corporate, of 14 Rue Royale, Paris 8e, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to cosmetic compositions for strengthening hair, in particular damaged hair.

As is well known, various treatments which are applied to hair have the effect of weakening the keratin of hair, thus making the latter more fragile and brittle. Amongst these chemical treatments, there may be mentioned in particular the operations of permanently waving hair which consist, firstly, of opening the S—S bonds of keratin with reducing compounds such as thioglycolic acid, ammonium thioglycollate, thioglycerol or thiolactic acid, and then of reforming these keratin bonds with oxidising agents, notably hydrogen peroxide or per-salts.

Other operations which weaken the keratin of the hair, include bleaching in particular with peroxides, which, in certain cases, can be very severe. The dyeing of hair, especially when this is repeated at regular intervals, also has the effect of damaging hair, and thus making it more fragile.

In addition to these chemical treatments, hair is also damaged by the action of atmospheric agents such as the sun and, more particularly, sea water.

In order to give hair which has been damaged in this way more strength and life, whilst improving the general appearance of the head of hair, a variety of treatments has been proposed. In particular, it has been proposed to treat hair with compositions based on proteins, more particularly protein hydrolysates. It has also been proposed to use compositions containing certain cationic polymers.

These various compositions certainly possess properties beneficial to the keratin of hair, providing, in particular, good protection against subsequent permanent waving, bleaching and dyeing, for example.

We have now found, according to the present invention, very surprisingly, that if, in the treatment of hair, certain cosmetic compositions containing a mixture of at least one cationic copolymer and at least one non-toxic salt of a divalent metal are used, it is possible, whilst protecting the hair, to impart excellent mechanical strength to it, (which can be measured by assessing the strength of the hair when it is elongated by 15% (Index I<sub>15</sub>)), a property of great importance in hair cosmetology, in a way which the compositions known previously did not make it possible to achieve to such a degree.

According to the present invention there is provided a cosmetic composition suitable for the treatment of hair, particularly damaged hair, for the purpose of improving its mechanical strength, which comprises a composition, which may be limpid and/or homogeneous, which comprises at least one cationic polymer possessing at least one, and preferably several, tertiary amine and/or quaternary ammonium groups, and at least one non-toxic salt of a divalent metal which is soluble in water or in 50/50 (by volume) aqueous-alcoholic solutions.

In addition to possessing excellent mechanical strength, hair treated by the compositions of this invention possesses purely cosmetic properties which are very noteworthy; thus the hair is pleasant to touch, attractively springy and has a shinier appearance. Moreover, subsequent wave-settings carried out after the treatment stay in well, the hair being supple and having attractive waves.

The cationic polymers which can be used according to the invention belong to a well known class of compounds; in general terms they possess tertiary amine or quaternary ammonium groups in their main chain or as substituents.

In general terms, the cationic polymers which can be used according to the present invention have an average molecular weight of between about 1,000 and 2,000,000.

Amongst the cationic polymers which can be used according to the invention, the following polymers may be mentioned in particular:

1) The quaternary derivatives of certain cellulosic ethers, for example the polymers formed by reacting a hydroxyethyl-cellulose (for example having a degree of substitution of hydroxyethyl groups of about 1.3) with the product of the reaction between, say, about 0.7 mol of epichlorohydrin and about 0.7 mol of trimethylamine per unit of substituted anhydro-glucose, the polymer having an average molecular weight of 200,000—230,000.

The hydroxyethyl-cellulose is made up of hydroxyethylated anhydroglucose units possessing variable degrees of hydroxyethylation. It can be prepared by reacting alkaline cellulose with ethylene oxide.

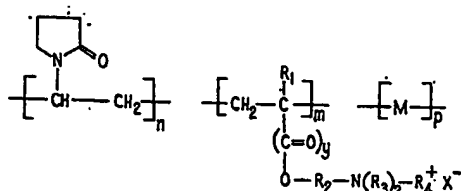
The degree of substitution by quaternary nitrogen groups should be sufficient for the molecular weight of the substituted hydroxyethyl-cellulose polymer to be between 2,000 and 3 million.

The cellulosic ether derivatives preferably used are those which are water-soluble, non-ionic and substituted by a short chain alkyl or hydroxyalkyl radical. These derivatives are, for example, methyl-, ethyl- and hydroxyethyl-cellulose.

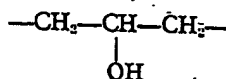
A commercially available quaternised derivative for use in the compositions of this invention is JR-1L or JR-400 sold by Messrs. Union Carbide. This polymer has a molecular weight of 100,000 to 1,000,000.

Quaternary derivatives of cellulosic ethers are, in particular, described in French Patent No. 1,492,597.

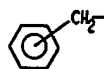
2) The quaternary copolymers of N-vinylpyrrolidone and another copolymerisable vinyl monomer. These copolymers can be represented as comprising recurring units of the formulae:



in which n indicates that from 20 to 99 mol % of the polymer consists of such recurring units, m indicates that from 1 to 80 mol % of the polymer consists of such recurring units, p indicates that from 0 to 50 mol % of the polymer consists of such recurring units and  $n+m+p=100$ , of the polymer,  $y=1$  or 0,  $\text{R}_1$  represents a hydrogen atom or  $-\text{CH}_3$ ,  $\text{R}_2$  the group



or  $-\text{C}_x\text{H}_{2x}-$ , with  $x=2$  to 18,  $\text{R}_3$ , a  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$  or t-butyl group,  $\text{R}_4$  a  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$  or



group, X a Cl, Br or I atom or a  $\text{SO}_3$ ,  $\text{HSO}_4$  or  $\text{CH}_3\text{SO}_3$  group and M represents a unit resulting from a copolymerisable vinyl monomer.

These quaternary copolymers can be prepared by copolymerisation of N-vinylpyrrolidone and a (lower)dialkylaminoalkyl (or hydroxyalkyl) acrylate (or methacrylate) and optionally, another copolymerisable vinyl monomer. The vinylpyrrolidone units represent 20 to 99 mol %, the units originating from a (lower) dialkylaminoalkyl (or hydroxyalkyl) acrylate (or methacrylate) constitute between 1 and 80 mol % and the units originating from the other copolymerisable vinyl monomer constitute between 0 and 50 mol %. The molecular weight of these copolymers is generally between

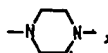
15,000 and 1,000,000, more particularly between 50,000 and 500,000. Polymers of this type include the copolymers known by the tradename Gafquat 734 and 755, sold by Messrs. GAF (the molecular weight of Gafquat 734 is about 100,000 and that of Gafquat 755 is greater than 1,000,000).

3) The copolymers which result from the polyaddition or polycondensation of piperazine or a derivative thereof with bi-functional compounds such as alkyl dihalides, dihalogenated derivatives, bis-halohydrins, bis-epoxides, epihalohydrins such as epichlorohydrin, bis-unsaturated derivatives such as divinyl-sulphone, unsaturated acids, diacids or diisocyanates or formaldehyde.

These copolymers can be represented by the formula:



in which A denotes a radical containing two secondary amino groups, and preferably the radical

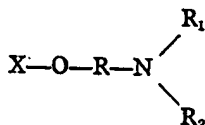


and Z denotes the symbol B or B'; B and B', which may be identical or different, each denotes a divalent radical which can be an alkylene radical with a straight or branched chain of up to 6 carbon atoms in the main chain and which can, in addition, possess oxygen, nitrogen and/or sulphur atoms and 1 to 3 aromatic or heterocyclic rings, it being possible for the oxygen, nitrogen and sulphur atoms to be present in the form of ether, thioether, sulphoxide, sulphone, sulphonium, amino, amino-oxide, quaternary ammonium, amido, imido, urea, alcohol, ester and/or urethane groups.

These copolymers have a molecular weight which is generally between 1,000 and 15,000.

Amongst these polymers, there may be mentioned, in particular, that obtained by poly-condensation of piperazine or epichlorohydrin, this polymer having a molecular weight of 1,500 to 3,000.

4) The cationic polymers of starch, such as those which can be represented by the following formula:



in which: X is starch, R is an alkylene or hydroxyalkylene radical and R<sub>1</sub> and R<sub>2</sub> each represents the same or different alkyl, aryl or aralkyl radical.

Such copolymers are described in, for example, United States Patents Nos. 2,813,093 and 3,186,911.

5) The copolymers resulting from the copolymerisation of 43 to 16% by weight of methyl methacrylate, 54 to 25% by weight of dimethylaminoethyl methacrylate and 12 to 52% by weight of octadecyl methacrylate. These copolymers can be used either in the form of the free base, or in quaternised or cross-linked form. In general terms, these copolymers have an average molecular weight of between about 10,000 and 1,500,000.

According to the present invention, the concentration of cationic copolymer in the composition is generally between 0.2 and 25%, preferably between 0.5 and 12%, by weight based on the total weight of the composition.

As stated above, the cosmetic compositions according to the invention contain, in addition to the cationic copolymer, at least one non-toxic salt of a divalent metal, including alkaline earth metals, which is soluble in water or in 50/50 aqueous-alcoholic solutions. Amongst the non-toxic salts of divalent metals which can be used, there may be mentioned, in particular, calcium, magnesium, manganese, iron, strontium, zinc and cadmium carbonates, silicates, nitrates, acetates, gluconates, pantothenates and lactates.

The concentration of these divalent metal salts in the compositions according to the invention is generally between 0.005 mol. and 0.05 mol, preferably about 0.01 mol, per gram of cationic copolymer.

The various comparative tests which we have carried out have shown unambig-

ously that the presence of at least one salt of a divalent metal is essential if one is to obtain significant improvements in the mechanical strength of hair. However the exact mechanism by which these divalent metal salts act has not yet been elucidated precisely.

The cosmetic compositions can be in various forms and, in particular, in the form of an aqueous, alcoholic or aqueous-alcoholic solution of an aliphatic alcohol such as ethyl alcohol or isopropyl alcohol, or they can be in the form of a cream, a gel or an emulsion, or in the form of a spray or aerosol foam.

The pH of the compositions according to the invention is generally between 3 and 9, preferably between 6 and 8.

According to a particular embodiment, the compositions are in the form of an aqueous, alcoholic or aqueous-alcoholic solution and form wave-setting lotions. In this embodiment, the concentration of cationic copolymer is generally between 1 and 3% by weight.

In addition to the cationic copolymer, the composition can, in this embodiment, contain other cosmetic resins, generally at a concentration of between 0.2 and 1%, "Cosmetic resins" are the resins which are used in cosmetic composition (see, for example, *Problem Capillaires*, pages 181 to 183, Gauthier-Villars, Paris 1966), particular mention may be made of: polyvinylpyrrolidone, generally of molecular weight between 10,000 and 70,000; 70:30% and 30:70% vinylpyrrolidone/vinyl acetate copolymers  $k$  value (1% ethanol solution) 25—50, copolymers of vinyl acetate and an unsaturated carboxylic acid such as crotonic acid (molecular weight about 20,000, for example); copolymers resulting from the copolymerisation of vinyl acetate (75—85%), crotonic acid (5—15%) and an acrylic or methacrylic ester (5—15%) or an alkyl vinyl ether (5—15%); copolymers resulting from the copolymerisation of vinyl acetate (63—88%), crotonic acid (5—15%) and (a) a vinyl ester of an acid with a carbon chain of 10—22 carbon atoms or (b) an allyl or methallyl ester of an acid with a carbon chain of 10—22 carbon atoms; copolymers resulting from the copolymerisation of an ester of an unsaturated alcohol of 2—12 carbon atoms and a saturated carboxylic acid with a carbon chain of 2—5 carbon atoms (65—80%), an unsaturated acid with a carbon chain of 4 to 12 carbon atoms (7—12%) and at least one ester of a saturated alcohol with a carbon chain of 8—18 carbon atoms and an unsaturated acid with a carbon chain of 4 to 12 carbon atoms (10—20%); and copolymers resulting from the polymerisation of at least one unsaturated ester and at least one unsaturated acid.

These compositions, which are in the form of an aqueous, alcoholic or aqueous-alcoholic solution, can also be mixed with a suitable amount of a propellant gas liquefied under pressure, such as dichlorodifluoromethane or trichlorofluoromethane and a mixture thereof and can thus form sprays or aerosol foams for the hair.

Alternatively, the cosmetic compositions can contain a detergent in addition to the cationic copolymer and the non-toxic salt, so that they are in the form of treatment shampoos. The detergents which can be used in such compositions can be anionic, non-ionic, cationic or amphoteric detergents.

Amongst the anionic detergents, there may be mentioned, in particular: alkyl sulphates, alkyl ether sulphates, alkyl polyether sulphates, alkyl sulphonates (the alkyl groups possessing 8 to 18 carbon atoms), fatty acid soaps, monosulphosuccinates of fatty alcohols, condensation products of fatty acids with isethionic acid, condensation products of fatty acids with methyltaurine, condensation products of fatty acids with sarcosine and condensation products of fatty acids with a protein hydrolysate.

Amongst the cationic detergents, there may be mentioned in particular: long chain quaternary ammonium compounds, esters of fatty acids and amino-alcohols and polyether amines.

Amongst the non-ionic detergents, there may be mentioned in particular: esters of polyols and sugars, condensation products of ethylene oxide with fatty acids, with fatty alcohols, with long chain alkyl-phenols, with long chain mercaptans and with long chain amides, and polyethers of polyhydroxylic fatty alcohols. Amongst the amphoteric detergents there may be mentioned in particular: asparagine derivatives, condensation products of monochloroacetic acid with imidazolines and alkylamino-propionates.

In the shampoo compositions, the concentration of detergent is generally between 5 and 50% and the concentration of cationic copolymer is generally between 3 and 25%, by weight based on the total weight of the composition, the proportion of non-toxic salt being the same as indicated above.

In this embodiment, the concentration of cationic copolymer should generally be higher than when the composition is, for example, in the form of a lotion, because, after application, the head of hair is rinsed immediately and this limits the contact time of the cationic copolymer with the hair.

In another embodiment, the compositions according to the invention can contain 1 to 10% by weight of one, and preferably several, natural aminoacids or protein hydrolysates, in addition to the cationic copolymer and the non-toxic salt. Amongst the natural aminoacids which can be used in this particular embodiment, there may be mentioned, in particular, the following: glycine, glutamic acid, aspartic acid, lysine, serine and alanine; these aminoacids are natural aminoacids which are found combined, in the form of polypeptides, in substances such as collagen, found in skins, bones and certain animal tissues, and certain keratin-containing substances. The protein hydrolysates used herein generally have an average molecular weight of less than 10,000 and preferably less than 2,000.

By "protein hydrolysate" as used herein, there are to be understood the products resulting from the hydrolysis of collagen (or gelatine) or keratin-containing substances such as horns, fingernails and hair, or other protein substances such as casein and albumins.

The initial hydrolysis of collagen gives rise to the formation of gelatine which is a protein of low molecular weight. On more vigorous hydrolysis especially using sodium hydroxide solution or sulphuric acid, protein hydrolysates are obtained. It should be noted that hydrolysis of collagen can, in certain cases, be carried out with certain enzymes.

Protein hydrolysates can also be obtained from the hydrolysis of certain keratin-containing substances, and, as in the case of collagen, this hydrolysis can be carried out by means of sodium hydroxide solution or sulphuric acid, but generally at lower temperatures, particularly in the case of sodium hydroxide solution, so as to avoid the degradation of the sulphur-containing aminoacids, especially methionine and cystine, which are constituents of keratin.

The compositions according to the invention can also contain other ingredients conventionally used in such cosmetics compositions, such as thickeners, for example alkanolamides of fatty acids, carboxymethyl-cellulose, hydroxymethyl-cellulose, esters of long chain polyols and natural rubbers, preservatives such as methyl *para*-hydroxybenzoate or propyl *para*-hydroxybenzoate, dyestuffs and perfumes.

The present invention also provides a process for the treatment of hair, particularly damaged hair, for the purpose of improving its mechanical properties and especially its strength, which comprises applying thereto a sufficient amount of a composition according to the invention.

When the composition according to the invention is in the form of a shampoo, the application may be followed by rinsing with water, the hair being dried thereafter.

When the composition according to the invention is in the form of a wave-setting lotion, after the composition has been applied, the hair may be wound up on wave-setting rollers and then dried by the external application of heat. After the rollers have been removed, excellent curls can be obtained, the hair being strong, shiny and soft to the touch.

The following Examples further illustrate the present invention.

#### EXAMPLE 1

A wave setting lotion is produced by making up the following mixture:

Polymer resulting from the polycondensation of piperazine and epichlorohydrin (M.W.=2,000)	2 g
60/40 vinylpyrrolidone/vinyl acetate copolymer. Value K, (as a 1% by weight solution in EtOH) 30—50	0.5 g
Calcium acetate	1.2 g
Ethyl alcohol	20 g
Perfume	0.1 g
Water, q.s.p.	100 g
The pH of this lotion is 8.7.	

This lotion is applied to damaged hair which has been bleached and permanently waved several times.

After having washed the head of hair using a shampoo and then rinsed the hair, the above lotion is applied for several minutes, and the hair is then wound up on wave-setting rollers and dried under a hood at a temperature of the order of 40 to 60°C. After drying, the rollers are removed and it is found that the hair has a good wave and is shinier and much stronger than before.

In this Example, the calcium acetate can advantageously be replaced by the corresponding molar quantity of Fe(II) acetate.

#### EXAMPLE 2

A gel for the treatment of damaged hair is prepared by making up the following mixture:

5	50% by weight solution in ethanol of		5
	Gafquat 734 sold by Messrs. GAF		
	(quaternary copolymer of polyvinyl-		
10	pyrrolidone, average molecular		10
	weight 100,000)	5 g	
	Calcium acetate	1.6 g	
	"Cellosize" (hydroxyethyl-		
	cellulose)	1.25 g	
15	Dyestuff	0.2 g	
	Water, q.s.p.	100 g	15
	The pH of this composition is 8.		

After having washed and rinsed hair which has previously been permanently waved and dyed several times, the above gel is applied, impregnating the head of hair well. This treatment makes it possible to give back a natural appearance to the head of hair, the hair being more pleasant to the touch, shinier and much stronger.

If the calcium acetate in the above Example is replaced by the corresponding molar amount of zinc acetate or cadmium acetate, the same result is obtained, that is to say a general improvement in the mechanical properties of the hair.

#### EXAMPLE 3

A lotion for the treatment of damaged hair is produced by making up the following mixture:

25	50% by weight solution in ethanol			25
	of Gafquat 734 sold by Messrs.			
	GAF (quaternised copolymer of			
30	polyvinylpyrrolidone, average			30
	molecular weight 100,000)	2.5 g		
	Protein hydrolysates resulting from			
	the complete hydrolysis of collagen	1 g		
35	Calcium gluconate	3 g		
	Cetyl-trimethyl-ammonium bromide	0.1 g		
	Water, q.s.p.	100 g		35
	The pH of this composition is 7.6.			

After having washed bleached hair using a shampoo, the hair is rinsed and then the lotion is applied for several minutes to the hair. The hair is then dried, optionally after having set it in waves. After this treatment, it is found that the hair has regained its natural appearance, is shinier, softer to the touch and much stronger than before.

In this Example, it is possible to replace the calcium gluconate by the corresponding molar amount of calcium lactate or calcium pantothenate and obtain the same effects.

#### EXAMPLE 4

A wavesetting lotion for the treatment of damaged hair is produced by making up the following mixture:

50	Polymer resulting from the			
	polycondensation of piperazine			
	and epichlorohydrin			
	(M.W.=2,000)	0.5 g		50
	Glycine	5 g		
	Manganese acetate	1.8 g		
55	Water-soluble perfume	0.1 g		
	Propyl p-hydroxybenzoate	0.3 g		
	Cetyl-stearyl alcohol oxyethylenated			55
	with 15 mols of ethylene			
	oxide per mol of alcohol	0.3 g		
60	Water, q.s.p.	100 g		
	The pH of this composition is 6.7.			60

This lotion is applied to damaged hair which has been bleached several times. After having washed the head of hair using a conventional shampoo and then having rinsed the hair, the above lotion is applied for 5 to 10 minutes; the hair is then wound up on wavesetting curlers (15—25 mm) and dried under a hood at a temperature of 35—45°C.

After drying, the curlers are removed; an excellent set is thus obtained, the hair having attractive waves and being soft to the touch. Moreover, it is less brittle.

#### EXAMPLE 5

A wavesetting lotion for the treatment of hair which has been badly damaged by chemical treatment is produced by making up the following mixture:

Quaternary derivative of cellulose  
ethers (known by the trade-  
name of JR—400 sold by  
Messrs. Union Carbide)

Glycine	1 g
Strontium acetate	5 g
Cetyl-trimethyl-ammonium chloride	2.5 g
Methyl <i>p</i> -hydroxybenzoate	0.5 g
Water-soluble perfume	0.3 g
Ethyl alcohol	0.2 g
Dyestuff	10 g
Water, q.s.p.	0.1 g
	100 g

The pH of this composition is 5.9.

When this lotion is applied under the same conditions as in the preceding Example, an excellent set, the hair being supple and soft to the touch, is obtained.

#### EXAMPLE 6

A treatment gel for strengthening damaged hair is produced by making up the following mixture:

50% by weight solution in ethanol  
of Gafquat 734 sold by Messrs.  
GAF (quaternary copolymer of  
polyvinylpyrrolidone, average  
molecular weight 100,000)

Protein hydrolysates resulting from  
the complete hydrolysis of collagen

Hydroxyethyl-cellulose	5 g
Mg silicate	5 g
Methyl <i>p</i> -hydroxybenzoate	2 g
Water-soluble perfume	1.6 g
Water, q.s.p.	0.5 g
	0.2 g
	100 g

The pH of this composition is 7.1.

After having washed and rinsed bleached hair, an appropriate amount of the above composition is applied to the head of hair to impregnate it completely; the composition is left to act for about 5 to 10 minutes. The hair is then rinsed with water and dried, optionally after having set it on wave-setting rollers.

By this treatment, hair having a very good appearance, which possesses all the physical characteristics of natural hair which has not previously undergone any damaging treatment, is obtained.

## EXAMPLE 7

A treatment emulsion for hair which has been weakened by numerous bleachings is produced by making up the following mixture:

5	Cetyl-stearyl alcohol	3.3 g	
	Lanolin alcohol oxyethylenated		5
	with 20 mols of ethylene oxide		
	per mol of alcohol	0.7 g	
10	20% by weight aqueous solution of		
	Gafquat 755 sold up Messrs.		
	GAF (quaternary copolymer of		10
	polyvinylpyrrolidone, average		
	molecular weight greater		
	than 1,000,000)	1 g	
15	Protein hydrolysates resulting from		
	the complete hydrolysis of collagen	5 g	15
	Wheat germ oil	1 g	
	Calcium gluconate	4.5 g	
	Methyl p-hydroxybenzoate	0.3 g	
20	Water-soluble perfume	0.2 g	
	Water, q.s.p.	100 g	20
	The pH of this composition is 5.6.		

When this emulsion is applied under the conditions of Example 6, it also strengthens the hair very well, although it is neither limpid nor homogeneous.

A similar result is obtained when the calcium gluconate in this composition is replaced by the corresponding molar amount of magnesium lactate or zinc lactate.

## EXAMPLE 8

A shampoo for the treatment of damaged hair is produced by making up the following mixture:

30	Triethanolamide lauryl sulphate	7 g	
	20% by weight aqueous solution of		
	Gafquat 755	15 g	30
	Protein hydrolysates resulting from		
	the complete hydrolysis of collagen	3 g	
35	Calcium acetate	2 g	
	Water, q.s.p.	100 g	35
	The pH of this composition is 7.		

This shampoo is applied to damaged hair, leaving it to act on the hair for about 5 to 10 minutes; after rinsing the hair with water, the latter is dried, optionally after having wound it up on wavesetting curlers; hair which possesses all the characteristics of natural hair is obtained.

In the above composition, it is possible to replace the calcium acetate by the corresponding molar amount of calcium nitrate.

## EXAMPLE 9

A gel for the treatment of damaged hair is produced by making up the following mixture:

45	Quaternary copolymer resulting from		45
	the copolymerisation of 43% by		
	weight of methyl methacrylate,		
50	14% by weight of octadecyl meth-		
	acrylate and 43% by weight of		50
	dimethylaminoethyl methacrylate		
	crosslinked by means of diethylene		
	glycol methacrylate and quaternised		
55	by means of dimethyl sulphate		
	(Molecular weight: 1,200,000)	2.5 g	55
	Calcium acetate	1.6 g	
	Hydroxyethyl-cellulose	1.25g	
	Dyestuff	0.2 g	
60	Water, q.s.p.	100 g	
	The pH of this composition is 6.		



After having washed and rinsed hair which has been permanently waved and dyed several times, the above gel is applied, impregnating the head of hair well; this treatment makes it possible to give a natural appearance back to the hair, the hair being more pleasant to the touch, shinier and much stronger.

5 WHAT WE CLAIM IS:—

1. A composition suitable for the treatment of hair, which comprises at least one cationic polymer possessing at least one tertiary amine and/or quaternary ammonium group and at least one non-toxic salt of a divalent metal, which salt is soluble in water and/or a 50/50 (by volume) aqueous alcoholic solution. 5
2. A composition according to claim 1 in which the cationic polymer has an average molecular weight of between 1,000 and 2,000,000. 10
3. A composition according to claim 1 or 2, in which the cationic polymer is a quaternary derivative of a cellulosic ether; a quaternary copolymer of N-vinylpyrrolidone, and a dialkylaminoalkyl group-containing monomer, a polyaddition or polycondensation copolymer of piperazine or a derivative thereof and a difunctional compound; a cationic copolymer of starch, or a copolymer derived from 43 to 16% by weight of methyl methacrylate, 54 to 25% by weight of dimethylaminoethyl methacrylate and 12 to 52% by weight of octadecyl methacrylate. 15
4. A composition according to claim 1 or 2 in which the cationic copolymer is one specifically identified herein. 20
5. A composition according to any one of the preceding claims in which the non-toxic salt is a divalent calcium, magnesium, manganese, iron, strontium, zinc or cadmium carbonate, silicate, nitrate, acetate, gluconate, pantothenate or lactate. 25
6. A composition according to any one of the preceding claims which is in the form of an aqueous, alcoholic or aqueous-alcoholic solution, a cream, a gel or an emulsion. 25
7. A composition according to any one of the preceding claims in which the cationic copolymer is present in an amount between 0.2 and 25%, by weight based on the total weight of the composition. 30
8. A composition according to claim 7 in which the cationic copolymer is present in an amount between 0.5 and 12% by weight based on the total weight of the composition. 30
9. A composition according to any one of the preceding claims in which the metal salt is present in an amount between 0.01 mol and 0.5 mol per gram of cationic copolymer. 35
10. A composition according to any one of the preceding claims which has a pH between 3 and 9. 35
11. A composition according to any one of the preceding claims, which also contains between 0.2 and 1% by weight of a cosmetic resin. 40
12. A composition according to any one of the preceding claims which also contains a propellant gas liquefied under pressure. 40
13. A composition according to claim 12 in which the gas is dichlorodifluoromethane or trichlorofluoromethane or a mixture thereof. 45
14. A composition according to any one of claims 1 to 10 which also contains an anionic, nonionic, cationic or amphoteric detergent. 45
15. A composition according to any one of claims 1 to 7, 9 and 10 which also contains an anionic, non-ionic, cationic or amphoteric detergent in an amount between 5 and 50% by weight, the cationic copolymer being present in an amount between 3 and 25% by weight, based on the total weight of the composition. 50
16. A composition according to any one of the preceding claims which also contains from 1 to 10% of at least one amino acid or protein hydrolysate. 50
17. A composition according to claim 16 in which the amino acid is glycine, glutamic acid, aspartic acid, lysine, serine or alanine. 55
18. A composition according to Claim 16 in which the protein hydrolysate has an average molecular weight of less than 10,000. 55
19. A composition according to claim 18 in which the protein hydrolysate has an average molecular weight of less than 2,000. 60
20. A composition according to any one of claims 1 to 19 which also contains at least one thickener, preservative, dyestuff or perfume. 60
21. A composition according to claim 1 substantially as hereinbefore described. 60
22. A composition according to claim 1 substantially as described in any one of the Examples. 60
23. A process for treating hair, which comprises applying thereto a composition as claimed in any one of claims 1 to 22.

24. A process according to claim 23 in which the head of hair is subsequently rinsed and then dried.

25. A process according to claim 23 in which the hair is subsequently wound up on wavesetting rollers and the hair is dried with the application of heat.

26. A process according to claim 23 substantially as hereinbefore described.

27. A process according to claim 26 substantially as described in any one of the Examples.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.